

The University of Chicago

Founded by JOHN D. ROCKEFELLER

On the Nature of the Oxyazo Compounds

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS
OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By WILLIAM McPHERSON.

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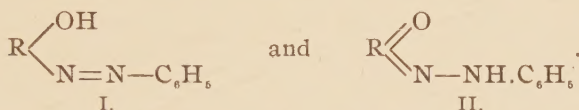
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ON THE NATURE OF THE OXY- AZO COMPOUNDS.

BY WILLIAM MCPHERSON.

The oxyazo compounds have been under investigation for the past fifteen years, especially because no decisive conclusion has been reached as to their constitution. Two general formulæ have been assigned to them; *viz.*,



According to the first of these, they are true oxyazo bodies; the second represents them as derivatives of quinones; *viz.*, quinonehydrazones. Goldschmidt, in consequence of results obtained with his students in the case of ortho- and paraoxyazo derivatives decided¹ that these compounds must all be regarded as monohydrazones of quinones or diketones. This conclusion, however, is not in accord with his own previous results obtained with phenyl isocyanate.² On the other hand, Jacobson,³ Meldola,⁴ Witt and Schmidt,⁵ Noeltig and Grandmougin,⁶ working chiefly with alkylated substitution-products or in the ortho series, came to conclusions directly opposite to those reached by Goldschmidt.

¹ Goldschmidt and Brubacher: Ber. d. chem. Ges., **24**, 2300; Goldschmidt and Pollak: *Ibid.*, **25**, 1324.

² Goldschmidt and Rosell: *Ibid.*, **23**, 487.

³ *Ibid.*, **25**, 992; **26**, 681; and **27**, 2700.

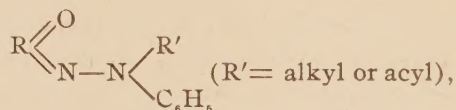
⁴ J. Chem. Soc., **53**, 460; **55**, 114 and 603; **59**, 372-710; **63**, 923; **65**, 834.

⁵ Ber. d. chem. Ges., **25**, 1013.

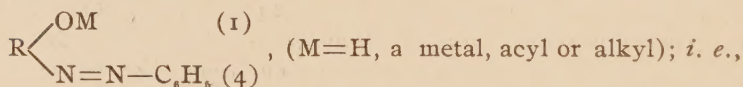
⁶ *Ibid.*, **24**, 1592.

The oxyazo compounds may conveniently be divided into two classes; namely, those belonging to the ortho series and those belonging to the para series. It does not of necessity follow that the compounds of the one series possess a constitution analogous to that of the other.

In order to attack this problem from an entirely new standpoint, I undertook, at the suggestion and under the direction of Dr. J. U. Nef, the study of the action of unsymmetrical alkylated and acylated derivatives of phenylhydrazine on various quinones, both of the ortho and the para series. The condensation-products thus obtained,

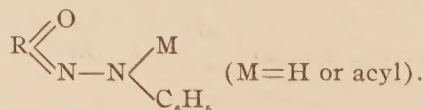


were compared with the free oxyazo compounds and the corresponding products obtained from these by direct alkylation and acylation.¹ The results are decisive; they prove that all paraoxyazo compounds, their salts as well as the acylated and alkylated substitution-products, possess the general formula

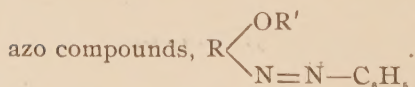


all are true oxyazo compounds.

The work in the ortho series, while not so decisive nor so exhaustive, all points now to one conclusion; namely, that these compounds and their acylated substitution-products are monohydrazones of orthodiketones,

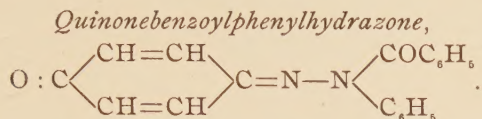


The alkylated substitution-products, on the other hand, are



¹ A preliminary notice of my results appeared in the Ber. d. chem. Ges., 28, 2414.

I. THE ACTION OF α -ACYLATED PHENYLHYDRAZINES ON PARAQUINONES.



Benzoquinone and its homologues react with phenylhydrazine with evolution of nitrogen and formation of resinous products.¹ Since hydroxylamine² and its α -alkylated substitution-products³ react in a normal manner with quinone, it seemed possible that a replacement of the imide hydrogen in phenylhydrazine by acyl or alkyl might give rise to products which would condense in a normal manner with paraquinones; whereas, it was found that α -methyl and α -benzyl-

phenylhydrazine, $\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CH}_3 \end{array} \text{N}-\text{NH}_2$ and $\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_7\text{H}_7 \end{array} \text{N}-\text{NH}_2$, react

with benzo-, toluo-, and thymoquinone with formation of hydroquinone and tetrazones (see below); α -naphthoquinone reacts, just as with phenylhydrazine itself in a perfectly normal manner with these reagents. All these quinones, however, give normal condensation-products on treatment with α -acylated phenylhydrazines.

One and two-tenths grams of α -benzoylphenylhydrazine hydrochloride, made according to the directions of Widman,⁴ were dissolved in 300 cc. of water containing a few drops of hydrochloric acid. To this was added a solution of 0.5 gram benzoquinone in 200 cc. of water. A yellow precipitate begins to separate out at once and, after two hours, the reaction is completed. Yield 1.3 grams (theory 1.4 grams). The substance was purified by recrystallizing twice from benzene, in which it readily dissolves while hot and from which it is deposited on cooling in yellow, flat needles or in prisms melting at 171°.

0.1870 gram substance gave 15.5 cc. nitrogen at 24.5° and 744.8 mm.

¹ Zincke : Ber. d. chem. Ges., **16**, 1563.

² Goldschmidt : *Ibid.*, **17**, 213.

³ Bridge : Ann. Chem. (Liebig), **277**, 90, 95.

⁴ Ber. d. chem. Ges., **26**, 945.

0.1961 gram substance gave 0.5410 gram CO_2 , and 0.0900 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2$.	Found.
C	75.49	75.22
H	4.63	5.10
N	9.29	9.15

Quinonebenzoylphenylhydrazone is very difficultly soluble in cold ether and alcohol. It separates out from hot alcohol in groups of crystals resembling sodium chloride; if the solution, however, is cooled very slowly, heavy, transparent, reddish-yellow crystals with numerous well-defined facets are obtained. The substance is readily soluble in chloroform and glacial acetic acid, moderately soluble in cold benzene, and insoluble in ligroin, and can therefore also be purified by crystallizing from a mixture of benzene and ligroin.

Behavior towards Reducing Agents.

Quinonebenzoylphenylhydrazone (1 gram) treated in cold acetic acid solution with zinc dust is split, in a few minutes, quantitatively into benzanilide and paramidophenol; on addition of water to the filtered solution, benzanilide separates out in plates (0.55 gram). These were purified by distillation and subsequent crystallization from alcohol. Yield, 0.3 gram of pure product melting at 161° .

0.2454 gram substance gave 16.1 cc. nitrogen at $26^\circ.2$ and 743.8 mm.

	Calculated for $\text{C}_{13}\text{H}_{11}\text{NO}$.	Found.
N	7.11	7.15

The presence of paramidophenol in the filtrate was established, after precipitating the zinc with hydrogen sulphide, by converting it into the hydrochloride and then by means of calcium hypochlorite¹ into quinonechlorimide; melting-point found, 85° .

This decomposition, which was also established in the case of the corresponding derivatives of toluo-, thymo-, and α -naphthoquinone, is entirely analogous to those observed by Goldschmidt² in the reduction of a whole series of acetyl and ben-

¹ Fogh: Ber. d. chem. Ges., **21**, 890.

² Ibid., **24**, 2300, and **25**, 1324.

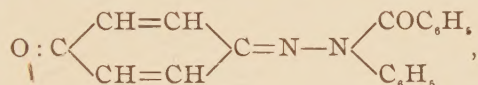
zoyl derivatives of orthooxyazo compounds both in the benzene as well as in the naphthalene series. This proves that the conclusions drawn by him from those results, *viz.*, that the acyl groups are bound to nitrogen and not to oxygen are entirely justifiable.

Behavior towards Phenylhydrazine.

Quinonebenzoylhydrazone reacts on addition of phenylhydrazine with such explosive violence that complete charring takes place. Even in dilute alcoholic or acetic acid solutions, decolorization, with decided evolution of heat and of nitrogen, takes place. This substance therefore behaves towards this reagent in a manner analogous to quinone and its homologues.

Comparison with Goldschmidt's so-called Quinonebenzoylphenylhydrazone.

The quinonebenzoylphenylhydrazone described above, which, from its method of synthesis and its properties, unquestionably possesses the constitution,

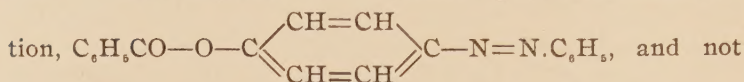


is *isomeric, not identical*, with the benzoyl derivative which can be obtained from paraoxyazobenzene by means of Baumann's reaction, or directly by heating it with benzoic anhydride. The benzoate of paraoxyazobenzene melts at 138° and crystallizes from alcohol, as was observed in a preparation made according to Tschirwinsky's directions,¹ in thin, voluminous, yellow plates or scales. Zinc and acetic acid convert it into the colorless dihydride described by Goldschmidt and Brubacher² (melting-point found, 172°.5). This compound is readily converted, as I have observed, by adding ferric chloride or mercuric oxide to its alcoholic solution, back again into the yellow benzoate of paraoxyazobenzene. Tschirwinsky's benzoate of paraoxyazobenzene is furthermore split in the cold by treatment with concentrated sulphuric acid or with alcoholic potash into benzoic acid and paraoxyazoben-

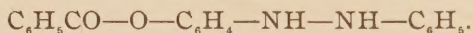
¹ Ber. d. chem. Ges., 6, 561.

² *Ibid.*, 24, 2302; and 25, 1325.

zene. This compound must therefore possess the constitution,



the isomeric formula given it by Goldschmidt and Brubacher; its dihydride, discovered by Goldschmidt and Brubacher, is therefore the corresponding hydrazo derivative,



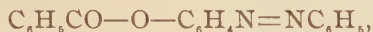
Goldschmidt has indeed given all the acetyl and benzoyl derivatives of paraoxyazo compounds the quinonehydrazone formula, *i. e.*, he assumes that the acyl group introduced is bound to nitrogen and not to oxygen. He was never able, however, to bring forward decisive experimental proof for this assumption in the case of paraoxyazo compounds. He never succeeded, for example in establishing a splitting of these compounds into acetanilide or benzanilide, respectively, as he had done in the case of the orthooxyazo compounds. His conclusions were therefore based chiefly on the conviction that all oxyazo compounds, the ortho as well as the para, must possess an analogous constitution, a conclusion which, as is now evident, was not justifiable.

A comparison of the quinone derivatives obtained by means of α -benzoylphenylhydrazine, from toluo-, thymo-, and α -naphthoquinone, with the corresponding benzoates from benzeneazoorthocresol, benzeneazothymol, benzeneazo- α -naphthol, in like manner establishes that the products are isomeric and not identical (see below).

Behavior of Quinonebenzoylphenylhydrazone towards Saponifying Agents.

The behavior of the actual quinonebenzoylphenylhydrazone towards concentrated sulphuric acid and alcoholic potash is very interesting. It is split, after standing in the cold, quantitatively into benzoic acid and paraoxyazobenzene. The same result is obtained on adding dilute hydrochloric acid to a hot alcoholic solution of the substance. The experiment was carried out in every case with 0.5 gram of material and the paraoxyazobenzene obtained very carefully compared with

a preparation made in the ordinary manner. All products melted at 152° and crystallized from benzene in peculiar flat crystals grouped together. Furthermore, they were all converted by means of Baumann's reaction into the ordinary benzoylated paraoxyazobenzene,



of Tschirwinsky (melting-point observed, 138° , thin plates).

These experiments prove that, on saponification, quinone-benzoylphenylhydrazone, as well as its isomer, the benzoate of paraoxyazobenzene, give one and the same product; *viz.*, paraoxyazobenzene, $\text{OH—C}_6\text{H}_4\text{N}_2\text{—C}_6\text{H}_5$. That this substance possesses a constitution represented by its name, that it is not quinonephenylhydrazone,



or a tautomeric compound, the following facts establish beyond a reasonable doubt:

1. Paraoxyazobenzene, by direct acylation or alkylation, gives acyl as well as alkyl derivatives, which unquestionably and exclusively contain the acyl as well as the alkyl group bound to oxygen, $\text{C}_6\text{H}_5\text{—N}_2\text{—C}_6\text{H}_4\text{—OM}$ ($\text{M}=\text{acyl or alkyl}$). This is proved in the case of the acyl derivatives by the experiments described in this paper, and in the case of the alkyl derivatives by the experiments of Jacobson.¹

2. The orthooxyazo derivatives by direct acylation give products which as unquestionably contain the acyl group

bound exclusively to nitrogen, $\text{R} \begin{array}{c} \text{O} \\ \text{N} \end{array} \text{—N} \begin{array}{c} \text{A} \\ \text{C}_6\text{H}_5 \end{array}$ (Goldschmidt

and others).

3. The free paraoxyazo compounds do not react, as I have observed, in the case of paraoxyazobenzene and others, with phenylhydrazine, either directly or in alcoholic solution, even if heated to 100° , whereas all paraquinonebenzoylphenylhydrazone derivatives, like benzoquinone itself, react with this reagent with explosive violence. Were oxyazobenzene identical with quinonehydrazone, $\text{O : C}_6\text{H}_4\text{=N—NH—C}_6\text{H}_5$, it is

¹ *Loc. cit.*

difficult to understand its indifference to phenylhydrazine as compared with the intense activity of its nitrogen-acylated derivatives.

4. The paraoxyazo compounds are all freely soluble in dilute caustic alkalies and in some cases even in dilute alkaline carbonates; in marked contrast is the behavior of the orthooxyazo compounds of the naphthalene series which are unquestionably quinonehydrazones. Thus benzeneazo- β -

naphthol, $\text{C}_{10}\text{H}_8 \begin{array}{c} \text{O} \\ \parallel \\ \text{N.NH.C}_6\text{H}_5 \end{array} \begin{array}{c} (\beta) \\ (\alpha) \end{array}$, and β -naphthoquinone-

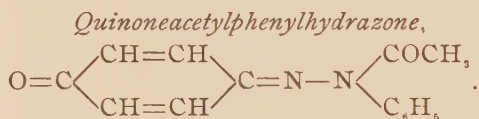
phenylhydrazone, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{O} \\ \parallel \\ \text{N.NH.C}_6\text{H}_5 \end{array} \begin{array}{c} (\alpha) \\ (\beta) \end{array}$, are insoluble in

and not affected by most concentrated caustic alkalies.¹ The

isomeric para compound, $\text{C}_{10}\text{H}_8 \begin{array}{c} \text{OH} \\ \diagup \\ \text{N}_2\text{C}_6\text{H}_5 \end{array} \begin{array}{c} (\alpha) \\ (\alpha') \end{array}$, which re-

markably enough is formed when α -naphthoquinone is treated with phenylhydrazine,² is, on the other hand, easily soluble even in alkaline carbonates. These noteworthy differences become self-evident if the paraoxyazo compounds are regarded as phenols.

5. A study of the physical properties of the free paraoxyazo compounds, carried out after my preliminary experiments, has led Auwers and Orton³ to results entirely in accord with those obtained by chemical methods.



The α -acetylphenylhydrazine used to prepare this compound was made from acetylformazylihydride according to Peckmann's directions⁴ and also by Widman's method.⁵ The latter method is more convenient. 0.5 gram of α -acetyl-

¹ Liebermann: Ber. d. chem. Ges., **16**, 2858; Zincke and Bindewald: *Ibid.*, **17**, 3031.

² Zincke and Bindewald: *Ibid.*, **17**, 3026.

³ Zeit. phys. Chem., **21**, 356.

⁴ V. Peckmann: Ber. d. chem. Ges., **27**, 1695.

⁵ Widman: *Ibid.*, **27**, 2964.

phenylhydrazine hydrochloride was dissolved in 25 cc. of water and acidified with a few drops of hydrochloric acid; to this was added a solution of 0.4 gram benzoquinone in 30 cc. of 10 per cent alcohol. Yellow crystals soon began to separate out; after half an hour these were filtered off and dried (yield, 0.58 gram). Recrystallized from a mixture of benzene and ligroin, the substance was obtained in flat, yellow needles melting at 118°.

0.2238 gram substance gave 24.2 cc. nitrogen at 25° and 743.3 mm.

0.1794 gram substance gave 0.4587 gram CO₂, and 0.0800 gram H₂O.

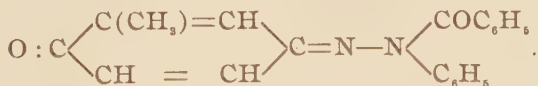
	Calculated for C ₁₄ H ₁₂ N ₂ O ₂ .	Found.
C	70.00	69.73
H	5.00	4.95
N	11.66	11.86

The substance is very soluble in benzene and chloroform, less so in alcohol and ether. It reacts violently with phenylhydrazine and is converted by alcoholic potash or concentrated sulphuric acid into paraoxyazobenzene. It is *isomeric*, *not identical*, with the acetate or paraoxyazobenzene,



which has been prepared by Wallach and Kiepenhauer;¹ the latter substance, prepared according to their directions, was found to crystallize from benzene-ligroin in plates melting at 89°.5, instead of 84°-85°, as given by these observers. Alcoholic potash splits it into paraoxyazobenzene and acetic acid.

Toluquinonebenzoylphenylhydrazone,



Toluquinone, 0.4 gram, dissolved in 120 cc. of dilute alcohol, was added to a solution of 1 gram α -benzoylphenylhydrazine sulphate in 180 cc. of 10 per cent alcohol. A yellow precipitate began to separate out at once. After two hours this was filtered off and recrystallized three times from benzene.

¹ Wallach and Kiepenhauer: Ber d. chem. Ges., 14, 2617.

0.1892 gram substance gave 0.5181 gram CO_2 , and 0.0921 gram H_2O .

0.1732 gram substance gave 13.9 cc. nitrogen at $23^\circ.5$ and 745 mm.

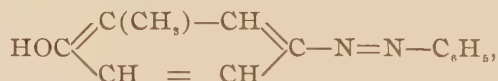
	Calculated for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$.	Found.
C	75.94	75.89
H	5.06	5.50
N	8.86	8.90

Toluquinonebenzoylphenylhydrazone is very soluble in ether and chloroform, moderately so in benzene, alcohol, and acetone. It separates from benzene or from benzene-ligroin in small, square, yellow tablets, melting at 151° . From alcohol it is deposited in red tablets or in yellow, feathery crystals. Treated with zinc dust and acetic acid, the hydrazone (0.5 gram) is split into benzanilide, melting-point 151° . A nitrogen determination gave the following result:

0.2132 gram substance gave 14.3 cc. nitrogen at 22° and 746 mm.

	Calculated for $\text{C}_{12}\text{H}_{11}\text{NO}$.	Found.
N	7.11	7.59

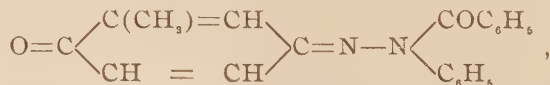
That the hydrazone has the constitution above given is proved by its method of synthesis and by its conversion, on treatment with alcoholic potash, into benzeneazoorthocresol,



obtained in yellow plates melting at 128° – 130° .

Comparison with Goldschmidt's So-called Toluquinonebenzoylphenylhydrazone.

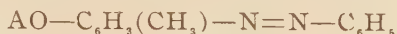
The compound described above, which from its method of synthesis and reactions must possess the constitution,



is *isomeric, not identical*, with the benzoate of benzeneazoorthocresol, first described by Noelting and Kohn,¹ and afterwards,

¹ Liebermann and Kostanecki: Ber. d. chem. Ges., **17**, 131, 879; Cf. Noelting and Kohn: *Ibid.*, **17**, 366.

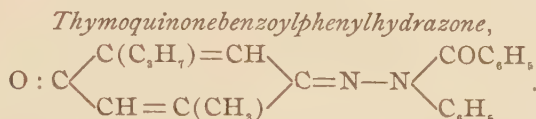
(as well as the corresponding acetate), regarded by Goldschmidt¹ as being a quinone derivative. The latter compound melts at 110°, and is split by alcoholic potash into benzene-azoorthocresol. Its dihydride melts at 142°, and is readily oxidized to the original benzoyl derivative by means of ferric chloride. It is evident therefore that the formula given by Goldschmidt to the acylated derivatives of benzeneazoorthocresol and their dihydrides must be changed to



and



respectively.



Four grams α -benzoylphenylhydrazine sulphate, dissolved in 350 cc. of 14 per cent alcohol, were added to a solution of 2 grams of thymoquinone in 300 cc. of 33 per cent alcohol. The mixture was heated until the quinone, partially precipitated, had redissolved and then allowed to stand twenty-four hours, when the yellow precipitate was filtered off. On examination this was found to be a mixture of two products, one yellow, the other colorless.² Their separation was accom-

¹ Ber. d. chem. Ges., 25, 1331.

² In the interaction between acylated hydrazines and quinones, it was generally found best to add a concentrated alcoholic solution of the quinone to an aqueous solution of the hydrazine salt whereby the quinone is at first precipitated in a finely divided condition. It was found, however, that if the reaction in the above instance was carried out in this way, the principal product was a crystalline substance, which is best purified by washing with small quantities of cold benzene, and then dissolving the insoluble part in hot benzene with addition of animal charcoal. On filtering and cooling, snow-white needles melting at 155° were obtained.

0.2030 gram substance gave 21 cc. nitrogen at 20°.5 and 736.4 mm.

0.1749 gram substance gave 17.7 cc. nitrogen at 19° and 736 mm.

0.1705 gram substance gave 0.4437 gram CO₂, and 0.0853 gram H₂O.

0.1730 gram substance gave 0.4512 gram CO₂, and 0.0868 gram H₂O.

	Calculated for C ₁₈ H ₁₄ N ₂ O ₂ .		Found.
C	70.86	70.96	71.12
H	5.51	5.56	5.56
N	11.02	11.40	11.31

Small amounts of a colorless substance were also obtained in the case of toluene and of α -naphthoquinone. Inasmuch as these seemed to have no particular bearing on the subject under investigation, no further study of them has yet been made, although it is my intention to examine them later.

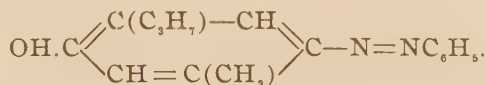
plished by repeated treatment with small amounts of cold benzene which dissolves only the yellow product; recrystallized from benzene-ligroin, the last-named substance was obtained in yellow plates melting at 132° .

0.1746 gram substance gave 13 cc. nitrogen at 23° and 745 mm.

0.1739 gram substance gave 0.4892 gram CO_2 , and 0.1003 gram H_2O .

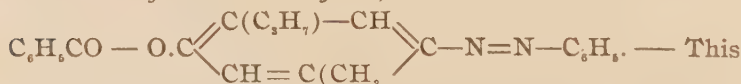
	Calculated for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2$.	Found.
C	77.09	76.71
H	6.14	6.41
N	7.82	8.20

Thymoquinonebenzoylhydrazone is very soluble in chloroform and benzene, moderately so in alcohol, and with difficulty in ether. Reduced with zinc dust and acetic acid in the cold, it is split into benzanilide, melting-point 163° . Saponified by means of alcoholic potash, it gives benzoic acid and benzeneazothymol,¹ melting-point 93° .



This, together with the method of synthesis, proves the constitution of the quinonehydrazone to be that given above.

Benzoate of Benzeneazothymol,



substance was prepared from benzeneazothymol by means of Baumann's reaction, in order to compare it with the isomeric quinone derivative just described. Recrystallized twice from hot alcohol, it was obtained in reddish-yellow needles melting at 115° . It is consequently *isomeric*, and *not identical*, with the product in question.

0.2195 gram substance gave 16.2 cc. nitrogen at 22° and 740 mm.

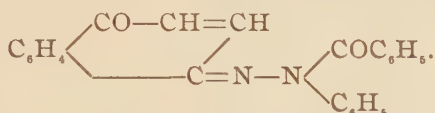
0.2081 gram substance gave 0.5881 gram CO_2 , and 0.1151 gram H_2O .

¹ Mazzari and Passetto : Gazz. chim. ital., 15, 53.

	Calculated for $C_{23}H_{22}N_2O_2$.	Found.
C	77.09	77.05
H	6.14	6.15
N	7.82	8.18

The benzoate of benzeneazothymol is very soluble in hot benzene and chloroform, moderately so in ether and ligroin. It is converted by means of alcoholic potash into benzoic acid and benzeneazothymol, whose melting-point was found to be 93° and not 85° – 90° , as given by Mazzari and Possetto.

α -Naphthoquinonebenzoylphenylhydrazone,



Two grams of α -naphthoquinone, dissolved in a small amount of alcohol, were poured into a liter of water, and thereupon an excess (5 grams) of α -benzoylphenylhydrazine sulphate, dissolved in 200 cc. of 40 per cent alcohol, added. The mixture was heated to 70° – 80° and then allowed to stand for twenty-four hours. The crude product, 4.5 grams, was purified by repeated crystallization from benzene-ligroin, and obtained in yellow silky needles, melting at $161^\circ.5$.

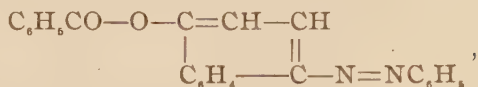
0.1848 gram substance gave 0.5312 gram CO_2 , and 0.0814 gram H_2O .

0.2641 gram substance gave 18.7 cc. nitrogen at 25° and 745.3 mm.

	Calculated for $C_{23}H_{16}N_2O_2$.	Found.
C	78.40	78.35
H	4.54	4.90
N	7.95	7.78

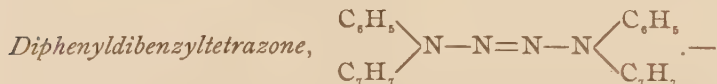
The substance is very soluble in benzene; it dissolves less readily in ether and alcohol, and is insoluble in ligroin. Reduced with zinc dust and acetic acid, it is split into benzanilide. Alcoholic potash converts it into benzeneazo- α -naphthol, melting-point 205° , from which was obtained the benzoate, melting-point $121^\circ.5$.

The benzoate of benzeneazo- α -naphthol,



has been prepared by Meldola;¹ it is *isomeric, not identical*, with the compound just described, and consequently must have its benzoyl group bound to oxygen. The formulæ given by Goldschmidt and Brubacher² to the acylated derivatives of α -naphthoquinonehydrazone or benzeneazo- α -naphthol and the corresponding dihydrides are therefore incorrect. The benzoate derivative can easily be prepared by Baumann's reaction, using barium hydroxide instead of sodium hydroxide. It is very slightly soluble in alcohol, ether, and hot ligroin, and always separates out in yellow needles melting at $121^\circ.5$. The two modifications described by Meldola were never observed.

II. ACTION OF α -ALKYLATED PHENYLHYDRAZINES ON PARA-QUINONES.



When benzoquinone and α -methylphenylhydrazine hydrochloride are brought together in dilute aqueous solution, an evolution of nitrogen is observed, and dimethyldiphenyltetrazone (melting-point 133°) separates out in leaflets (50 per cent of the calculated quantity).

Equimolecular proportions of benzoquinone and α -benzylphenylhydrazine sulphate (made by Widman's method) react at once in dilute aqueous solution; a strong odor of benzaldehyde is noticed and a bright yellow precipitate appears. After three hours' standing this was filtered off and purified by treatment in benzene solution with animal charcoal and repeated crystallization from benzene-ligroin. Colorless rhombohedra, melting with decomposition at 145° , were obtained. Philips³ mentions a substance melting at 109° , obtained by him from benzylphenylhydrazine by oxidation with

¹ J. Chem. Soc., **55**, 606.

² Ber. d. chem. Ges., **24**, 2313-14.

³ *Ibid.*, **20**, 2487.

mercuric oxide; no analysis is given and it is evident that the product was very impure.

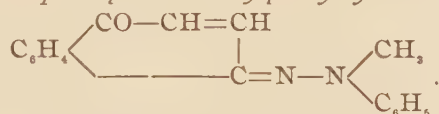
0.2040 gram substance gave 26.7 cc. nitrogen at 23° and 749.3 mm.

0.1648 gram substance gave 0.4822 gram CO₂, and 0.0895 gram H₂O.

	Calculated for C ₂₆ H ₂₄ N ₄ .	Found.
C	79.59	79.79
H	6.12	6.03
N	14.29	14.61

The action of α -alkylated phenylhydrazines on tolu- and thymoquinone is similar to that described in the case of benzoquinone.

α -Naphthoquinonemethylphenylhydrazone,



A solution of 5 grams of α -naphthoquinone in a small amount of alcohol was poured into a liter of water. To this was added a solution of 6 grams of α -methylphenylhydrazine sulphate in 200 cc. of 10 per cent alcohol. A slight evolution of gas was observed, and, after standing over night, a dark-red, very bulky precipitate appeared. The crude product, 6.2 grams, was purified by crystallizing three times from benzene-ligroin, and thus obtained in long, flat, amethyst-colored crystals which assume a metallic luster when powdered, and melt at 118°.5.

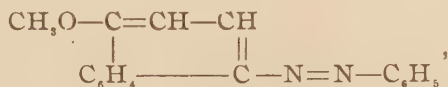
0.2398 gram substance gave 22.5 cc. nitrogen at 24° and 745 mm.

0.1550 gram substance gave 0.4404 gram CO₂, and 0.0765 gram H₂O.

	Calculated for C ₁₇ H ₁₄ N ₂ O.	Found.
C	77.86	77.48
H	5.34	5.48
N	10.68	10.40

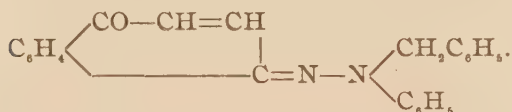
The quinonehydrazone is very soluble in benzene and chloroform, moderately so in alcohol and ether, and insoluble in

cold ligroin. The substance is *isomeric, not identical*, with the methyl ether obtained from benzeneazo- α -naphthol;¹ this compound, made according to the directions of Zincke and Bindewald, was separated from resinous products by means of cold ligroin, brown needles melting at 82°–83°. The latter compound must therefore possess the formula,



as has already been made probable by the experiments of Witt and Schmidt,² and others.

α -Naphthoquinonebenzylphenylhydrazone,



α -Naphthoquinone, 0.5 gram, dissolved in a small amount of alcohol, was poured into 300 cc. of water, and then a solution of 1 gram of α -benzylphenylhydrazine sulphate in 50 cc. of 10 per cent alcohol, which had been acidified with 2 cc. of strong sulphuric acid, was added. After standing over night, a tarry, dichroic mass had separated out which readily solidified when scratched. The product was obtained pure only after eight crystallizations from benzene-ligroin. It is very soluble in chloroform and benzene, sparingly soluble in alcohol and ether, and was obtained from benzene-ligroin in yellow, dichroic, flat needles, melting at 136°.

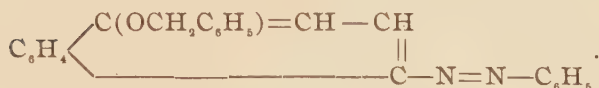
0.1998 gram substance gave 15.5 cc. nitrogen at 24° and 741.5 mm.

0.1876 gram substance gave 0.5632 gram CO₂, and 0.0962 gram H₂O.

	Calculated for C ₂₁ H ₁₈ N ₂ O.	Found.
C	81.65	81.80
H	5.30	5.55
N	8.26	8.52

¹ Zincke and Bindewald: Ber. d. chem. Ges., **17**, 3026.

² *Ibid.*, **25**, 1013

Benzyl Ether of Benzeneazo- α -naphthol,

An alcoholic solution of 5 grams benzeneazo- α -naphthol, prepared from α -naphthol and phenyldiazonium nitrate, was treated with 1.6 grams caustic soda and 5 grams benzyl chloride. The reaction was complete after five hours' heating. The product obtained was separated from some tar by recrystallizing from benzene-ligroin. It is very soluble in benzene but insoluble in ligroin. It consists of ruby-red, monoclinic crystals, which melt at 102° . When powdered, these become yellow.

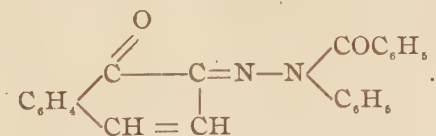
0.1962 gram substance gave 15.4 cc. nitrogen at $28^\circ.5$ and 748.8 mm.

0.2000 gram substance gave 0.6020 gram CO_2 , and 0.1020 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}$.	Found.
C	81.65	82.08
H	5.30	5.66
N	8.26	8.51

III. THE ACTION OF α -ALKYLATED AND OF α -ACYLATED PHENYLHYDRAZINES ON β -NAPHTHOQUINONEHYDRAZONE.

The Benzoate of β -Naphthoquinonephenylhydrazone is Identical with β -Naphthoquinonebenzoylphenylhydrazone,



The benzoyl derivative of β -naphthoquinonehydrazone can readily be prepared by adding benzoyl chloride to an alcoholic solution of the hydrazone, containing 1 molecule of sodium ethylate. Reaction takes place in the cold. The benzoate formed was purified by recrystallization from ben-

zene-ligroin. It forms yellow needles, melting at 191° , sparingly soluble even in hot alcohol, and fairly soluble in benzene.

0.2524 gram substance gave 18.6 cc. nitrogen at $24^{\circ}.5$ and 740.3 mm.

0.2080 gram substance gave 0.5983 gram CO_2 , and 0.0904 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_2$.	Found.
C	78.40	78.44
H	4.54	4.83
N	7.95	8.07

The substance is readily split into its components, benzoic acid and β -naphthoquinonehydrazone, melting-point 138° , by treatment either with alcoholic potash or with concentrated sulphuric acid.

It can also be prepared from the hydrazone by heating with benzoic anhydride to 150° for five hours.

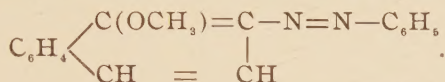
The corresponding acetate of β -naphthoquinonehydrazone has been prepared by Meldola¹ by means of acetic anhydride. This compound gives, according to Meldola, acetanilide on reduction with zinc dust and acetic acid. It can be obtained quantitatively, as I have found, by heating 5 grams of the hydrazone with 50 grams acetic anhydride and 20 grams fused sodium acetate for six hours at 100° .

That the benzoate of β -naphthoquinonehydrazone has the benzoyl group bound to nitrogen, is proved by its synthesis from β -naphthoquinone and α -benzoylphenylhydrazine sulphate. When these reagents are brought together in a dilute alcoholic solution, in a manner analogous to other cases described in this paper, a reaction takes place at once, even at 0° , with separation of a yellow precipitate. This product is so unstable that all attempts to purify it failed; after filtration it is rapidly converted into a tarry mass. If the reaction is effected at higher temperatures, however, a normal condensation results. Two grams of the sulphate were dissolved in 180 cc. of 20 per cent. alcohol, and heated to boiling. As soon

¹ J. Chem. Soc., 65, 839.

as the air is expelled from the flask, a solution of 1 gram of β -naphthoquinone in 50 cc. of alcohol, was slowly added, and the boiling continued for twenty minutes. A bright-yellow precipitate separates out which gradually becomes tarry; on decanting and washing with hot alcohol, the impurities dissolve and leave a yellow crystalline residue, which, after recrystallization from benzene-ligroin, was obtained in yellow needles, melting at 191° , and identical in all their properties with the benzoate of β -naphthoquinonehydrazone just described.

Methyl Ether of β -Benzeneazo- α -naphthol,



The experiments of Meldola and of Noelting and Grandmougin¹ with β -naphthoquinonehydrazone, have already made it highly probable that the ethers obtained from this compound, by means of alkalis and alkyl haloids, contain the alkyl group bound to oxygen. The following experiments confirm these conclusions.

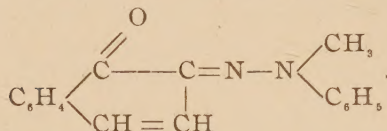
Two grams β -naphthoquinonehydrazone and 3 grams of methyl iodide were added to an alcoholic solution containing sodium methylate (from 0.5 gram sodium), and the mixture was heated to boiling for five hours. The methyl ether was precipitated by adding water and recrystallized several times from alcohol. It forms reddish-yellow plates readily soluble in benzene and hot alcohol, melting at 95° .

0.2234 gram substance gave 21.4 cc. nitrogen at 23° and 740 mm.

0.1622 gram substance gave 0.4609 gram CO_2 , and 0.0753 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$.	Found.
C	77.86	77.49
H	5.34	5.15
N	10.68	10.47

¹ Meldola: J. Chem. Soc., 65, 834; Cf. also Noelting and Grandmougin: Ber. d. chem. Ges., 24, 1592.

β-Naphthoquinonemethylphenylhydrazine,

Four grams of α -methylphenylhydrazine sulphate were dissolved in 500 cc. of water, containing 50 cc. of glacial acetic acid, and the mixture heated to 70° – 80° . Thereto were slowly added 3 grams of β -naphthoquinone, dissolved in a small amount of alcohol, and the temperature kept at 80° for two hours. On cooling, the condensation-product was filtered off and recrystallized, after treatment with animal charcoal, from benzene-ligroin. It formed yellow nodules, melting at 134.5° , very soluble in benzene, and sparingly soluble in hot alcohol, from which, on cooling, needle-shaped crystals are obtained. The yield is small, not more than 2 per cent.

0.1834 gram substance gave 17.2 cc. nitrogen at 22° and 742 mm.

0.1632 gram substance gave 0.4644 gram CO_2 , and 0.0797 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$.	Found.
C	77.86	77.60
H	5.34	5.42
N	10.68	10.41

From the facts presented in this paper, and from previous experiments by Goldschmidt, Meldola, and others, it follows that β -naphthoquinonehydrazine is a quinone derivative; it gives by direct acylation, or by treatment with benzoyl chloride and sodium ethylate, acylated derivatives in which the acyl group is unquestionably and exclusively bound to nitrogen. With alkyl iodides and alkalies, on the other hand, it is converted into alkyl ethers, in which the alkyl group is undoubtedly and exclusively bound to oxygen. It is highly probable from facts recorded in the literature that all ortho-oxyazo compounds show a similar deportment on acylation and alkylation.

